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MIXED HALODICYCLOPENTADIENYL-NIOBIUM(V) AND -TANTALUM(V)

A. ANTIÑOLO, M. FAJARDO, A. OTERO and P. ROYO

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Alcalá de Henares, Madrid (Spain)

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Summary

Oxidation of $(\eta^5\text{-}C_5H_5)_2MCl$ (M = Nb, Ta) with 1 mol of Cl_2, Br_2 or I_2 gives $(\eta^5\text{-}C_5H_5)_2MClX_2$, whereas the reaction with an excess of the halogen gives the cationic complexes $[(\eta^5\text{-}C_5H_5)_2MClX]^+ X_3^-$ (X = Br, I). Similar oxidation of $(\eta^5\text{-}C_5H_5)_2MCl_2$ with 0.5 mol of halogen gives $(\eta^5\text{-}C_5H_5)_2MCl_2X$ complexes, but if the halogen is used in excess cationic $[(\eta^5\text{-}C_5H_5)_2MCl_2]^+ X_3^-$ (X = Br, I; M = Ta and X = I, M = Nb) are obtained. All these complexes can also be obtained simultaneously by oxidizing $(\eta^5\text{-}C_5H_5)_4M_2Cl_3$, and the separation is fairly easy in most cases. Conductivity and IR and NMR data are discussed.

Introduction

Trihalodi-η^5-cyclopentadienyl complexes of niobium(V) and tantalum(V), $(\eta^5\text{-}C_5H_5)_2MX_3$ (X = Cl, Br) have usually been obtained from reactions of the metal pentahalides with NaC_5H_5, $Mg(C_5H_5)Br$ [1], [2] or $Mg(C_5H_5)_2$ [3]. A very low yield of $(\eta^5\text{-}C_5H_5)NbI_3$ was obtained from the reaction of $(\eta^5\text{-}C_5H_5)_2NbCl_2(OH)$ with NH_4I [4]. Only one derivative containing two different halogens is known, viz. $(\eta^5\text{-}C_5H_5)_2NbI_2Cl$, which was obtained [5] by reaction of $(\eta^5\text{-}C_5H_5)_2NbS_2Cl$ with MeI.

In order to add to this scanty knowledge of halodi-η^5-cyclopentadienyl complexes of niobium and tantalum and to ascertain the chemical behaviour of the dimers $(\eta^5\text{-}C_5H_5)_4M_2Cl_3$ [6], [7] (M = Nb (I), Ta (II)) we have carried out oxidation reactions with halogens, which provide simple routes to halodi-η^5-cyclopentadienyl neutral or cationic niobium(V) and tantalum(V) complexes, depending on the nature and the ratio of the halogen used.

Results and discussion

Synthetic studies

The reactions with chlorine always give the trichloro-derivatives $(\eta^5\text{-}C_5H_5)_2MCl_3$ (M = Nb, Ta), whatever be the ratio of halogen and starting complex $(\eta^5\text{-}C_5H_5)_2M^{III}Cl$, (M = Nb (III), Ta (IV)); $(\eta^5\text{-}C_5H_5)_2M^{IV}Cl_2$, (M = Nb (V), Ta (VI)) or $(\eta^5\text{-}C_5H_5)_2M^{III}Cl(\mu\text{-}Cl)ClM^{IV}(\eta^5\text{-}C_5H_5)_2$, (M = Nb (I), Ta (II)), see eqs. 1, 2, 3,

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4 in Scheme 1. However, in the case of the reaction shown in eq. 1, $(\eta^5\text{-}C_5H_5)_2MCl_2$ is simultaneously formed, as there is not enough halogen for complete oxidation. No cationic complexes can be obtained from these chloro complexes because of the instability of Cl_3^- and the low dissociation in solution of the neutral complexes.

When the oxidation of $(\eta^5\text{-}C_5H_5)_2M^{III}Cl$ is carried out using 1 mol of bromine, as indicated by eq. 2, the reaction gives new mixed M^V halo complexes which are formulated as $(\eta^5\text{-}C_5H_5)_2MClBr_2$, (M = Nb (VII), Ta (VIII)) on the basis of the analyses shown in Table 1.

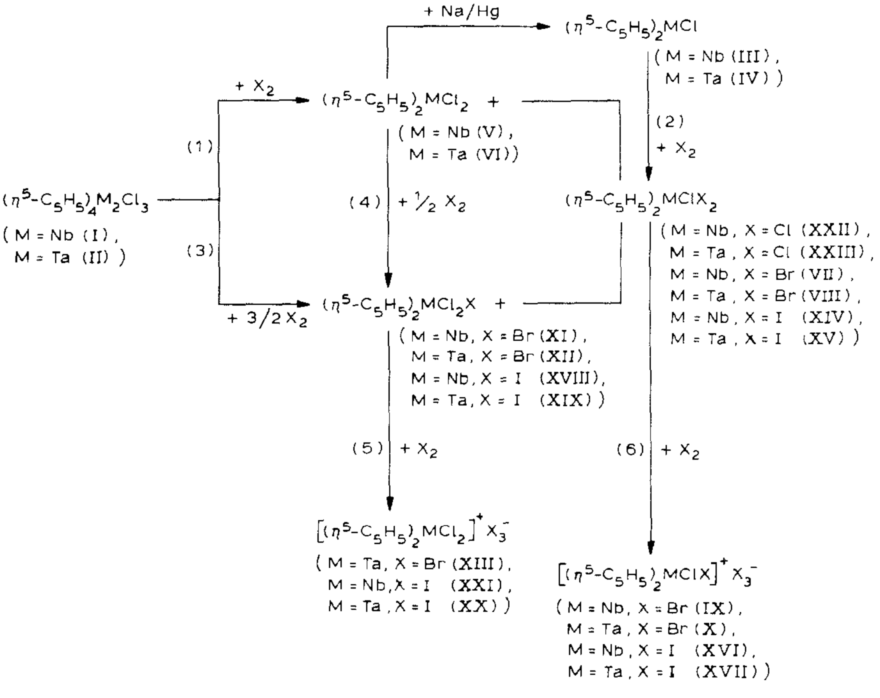
The same reaction with 2 mol or an excess of bromine in diethyl ether or THF gives new cationic complexes, as shown in eq. 6. These compounds give analyses corresponding to $[(\eta^5\text{-}C_5H_5)_2MBrCl]^+ Br_3^-$, (M = Nb (IX), Ta (X)).

The reactions of V and VI with 0.50 mol of bromine in diethyl ether under conditions shown by eq. 4 give the new neutral complexes $(\eta^5\text{-}C_5H_5)_2MCl_2Br$, (M = Nb (XI), Ta (XII)). When these reactions are carried out with an additional mol of bromine or a higher excess, as indicated in eq. 5, only the cationic tantalum complex $[(\eta^5\text{-}C_5H_5)_2TaCl_2]^+Br_3^-$ XIII is obtained; no reaction is observed for the niobium complex. This difference in behaviour can be explained on the grounds of the different dissociation of the neutral complexes, as discussed below.

The addition of 1 mol of bromine to the dimers I and II in THF as in eq. 1 leads to preferential oxidation of the M^{III} unit, without alteration of the M^{IV} unit, which remains in solution as $(\eta^5\text{-}C_5H_5)_2MCl_2$ and is easily separated from the less soluble complexes VII and VIII.

If the same reaction is carried out by addition of 1.5 mol of bromine, as in eq. 3, both M^{III} and M^{IV} units are oxidised to give a mixture of the monochlorodibromo

SCHEME 1



VII and VIII and dichloromonobromo XI and XII complexes. The two types of component are easily separated for both Nb and Ta because they have significantly different solubilities.

When the same reactions are carried out using an excess of bromine, dimer I gives IX along with smaller amounts of VII and XI, whereas dimer II gives only the cationic species X and XIII. This difference in behaviour is the result of the difference in solubilities and in the extent of the dissociation of the intermediate neutral complexes.

The addition of 1 mol of iodine to $(\eta^5\text{-}C_5H_5)_2MCl$, as in eq. 2, in diethyl ether or THF gives the two new mixed chloroiodo complexes $(\eta^5\text{-}C_5H_5)_2MClI_2$, (M = Nb (XIV), Ta (XV)), as formulated on the basis of their analytical compositions, shown

TABLE 1

ANALYTICAL DATA

Complex	Analyses (Found (calcd.) (%))		
	C	H	X[a]
(VII) $(\eta^5\text{-}C_5H_5)_2NbBr_2Cl$	27.94	3.17	24.93
	(28.71)	(2.41)	(25.42)
(VIII) $(\eta^5\text{-}C_5H_5)_2TaBr_2Cl$	23.99	2.37	20.92
	(23.72)	(1.99)	(21.01)
(IX) $[(\eta^5\text{-}C_5H_5)_2NbBrCl]^+ Br_3^-$	21.38	2.34	30.14
	(20.77)	(1.74)	(30.66)
(X) $[(\eta^5\text{-}C_5H_5)_2TaBrCl]^+ Br_3^-$	17.93	1.92	26.06
	(18.03)	(1.51)	(26.61)
(XI) $(\eta^5\text{-}C_5H_5)_2NbBrCl_2$	31.97	3.22	28.37
	(32.12)	(2.70)	(28.45)
(XII) $(\eta^5\text{-}C_5H_5)_2TaBrCl_2$	25.67	2.93	22.69
	(26.00)	(2.18)	(23.03)
(XIII) $[(\eta^5\text{-}C_5H_5)_2TaCl_2]^+ Br_3^-$	19.32	1.88	28.54
	(19.32)	(1.62)	(28.52)
(XIV) $(\eta^5\text{-}C_5H_5)_2NbClI_2$	23.81	2.01	20.56
	(23.44)	(1.97)	(20.78)
(XV) $(\eta^5\text{-}C_5H_5)_2TaClI_2$	19.34	1.74	17.73
	(20.00)	(1.68)	(17.72)
(XVI) $[(\eta^5\text{-}C_5H_5)_2NbClI]^+ I_3^-$	15.21	1.82	22.84
	(15.67)	(1.32)	(23.13)
(XVII) $[(\eta^5\text{-}C_5H_5)_2TaClI]^+ I_3^-$	13.80	1.90	20.39
	(14.06)	(1.18)	(20.75)
(XVIII) $(\eta^5\text{-}C_5H_5)_2NbCl_2I$	28.33	2.48	25.17
	(28.53)	(2.39)	(25.27)
(XIX) $(\eta^5\text{-}C_5H_5)_2TaCl_2I$	23.64	2.32	20.21
	(23.60)	(1.98)	(20.90)
(XX) $[(\eta^5\text{-}C_5H_5)_2TaCl_2]^+ I_3^-$	15.80	1.51	23.76
	(15.75)	(1.32)	(23.24)
(XXI) $[(\eta^5\text{-}C_5H_5)_2NbCl_2]^+ I_3^-$	17.96	1.98	26.24
	(17.80)	(1.49)	(26.27)
(XXII) $(\eta^5\text{-}C_5H_5)_2NbCl_3$	36.66	3.41	31.56
	(36.45)	(3.06)	(32.29)
(XXIII) $(\eta^5\text{-}C_5H_5)_2TaCl_3$	28.36	2.89	25.88
	(28.77)	(2.41)	(25.48)

[a] The total halogen present was determined and the total equivalents are expressed in % Cl. The presence of two different halogens was qualitatively determined.

in Table 1. If the reaction is carried out using an excess of iodine the two cationic species $[(\eta^5\text{-}C_5H_5)_2MClI]^+ I_3^-$ (M = Nb (XVI), Ta (XVII)) are formed, according to eq. 6.

Analogously the reaction of V and VI with 0.50 mol of iodine in diethyl ether gives the neutral complexes $(\eta^5\text{-}C_5H_5)_2MCl_2I$, (M = Nb (XVIII), Ta (XIX)) according to eq. 4. The reaction using one additional mol of iodine, as in eq. 5, gives the cationic complex $[(\eta^5\text{-}C_5H_5)_2TaCl_2]^+ I_3^-$ (XX); the analogous complex XXI of niobium is formed in this way in chloroform but not in diethyl ether.

The reaction of dimer I and II in the molar ratio indicated by eq. 1 leads to the selective oxidation of the M^{III} unit to give complexes XIV and XV along with unchanged $(\eta^5\text{-}C_5H_5)_2MCl_2$, which remains in solution. The same reaction with an excess of iodine gives cationic XVII and XX tantalum derivatives, whereas the niobium dimer produces solids of varying composition depending on the amount of halogen; these appear to contain a mixture of substances which could not be satisfactorily separated, and they were not further studied.

The behaviour indicated by eqs. 2 and 4 does not require any further comment. The oxidation of dimers I and II is consistent with their formulation as adducts of M^{III} and M^{IV} derivatives. The preferent oxidation of the M^{III} component is the result of the easier electrophilic attack of the halogen at the more electron rich metal atom.

The results obtained in reactions leading to the cationic complexes can be interpreted by taking into account the stability of the trihalide anion, the solubility relationships between the species formed in solution and their dissociation in the presence of polar solvents, as discussed below. Thus the instability of the Cl_3^- anion precludes the formation of cationic complexes by use of an excess of chlorine.

$[(\eta^5\text{-}C_5H_5)_2NbCl_2]^+ Br_3^-$ could not be obtained, probably due to the very low solubility and low dissociation of its precursor complex XI, whereas the reaction takes place easily with the tantalum complex XII, which is more soluble and much more dissociated.

The formation of the cationic complexes is easier using iodine as a consequence of the higher stability of the I_3^- anion, and the higher solubility and more extensive dissociation of the neutral precursor complex. This conversion is so easy that complex V gives directly XXI even with a deficiency of iodine in chloroform. The solid obtained by treating V in diethyl ether with an excess of iodine does not have the composition expected for XXI, but shows a low and variable content of carbon depending on the amount of iodine added. This is probably due to the formation of higher polyhalide anions, which is precluded in chloroform.

All the complexes are indefinitely stable under nitrogen as solids and in solution. The smaller the halogen the easier is the hydrolysis of the neutral complexes in the air, so that the iodo complexes can be stored unchanged. The cationic complexes are stable in the air. All are insoluble in most organic solvents and only slightly soluble in chloroform and acetone; the solubility is higher the larger the size of the halogen, so that the iodides are rather soluble, especially the diiodides. All the complexes are soluble in nitromethane.

All the complexes are diamagnetic at room temperature, as expected.

Conductivity measurements

The conductivity measurements are of special significance in interpretation of the chemical behaviour outlined above. The conductivities were measured in acetone except when the compound was insoluble and nitromethane had to be used. In this case, the extrapolated value of conductivity in acetone is included in Table 2 for comparison.

All the neutral complexes are partially dissociated as shown in the following equation:

$$(\eta^5\text{-}C_5H_5)_2MX_3 \rightleftarrows (\eta^5\text{-}C_5H_5)_2MX_2{}^+ + X^-$$

The values given in Table 2, show that the dissociation increases with increasing size of the halogen. The equivalent conductivity (ohm^{-1} mol^{-1} cm^2) is under 25 for the trichloro complexes $(\eta^5\text{-}C_5H_5)_2MCl_3$, around 45–50 for the dichloro complexes $(\eta^5\text{-}C_5H_5)_2MCl_2X$ (X = Br, I) and around 72–87 for the monochloro complexes $(\eta^5\text{-}C_5H_5)_2MClX_2$ (X = Br, I). It is noteworthy that XI has a low conductivity compared with XII, which has a very high conductivity in agreement with the different chemical behaviour observed.

All the cationic complexes show the characteristic conductivities expected for 1 : 1 electrolytes [8]. The very low solubilities of IX and X prevent the preparation of solutions of exactly known concentration, and so the observed conductivity values are omitted.

IR spectra

All the complexes show the characteristic absorptions for the $(\eta^5\text{-}C_5H_5)$ [9] ring at 3060–3070, 2920, 1435–1420, 1100, 1015–1005, 820 and 580 cm^{-1}. In the tantalum complexes the 820 cm^{-1} band is split into two bands located at 850 and 780 cm^{-1}.

TABLE 2

CONDUCTIVITY MEASUREMENTS IN ACETONE (nitromethane)[a]

Complex	Concentration ($mol\ l^{-1} \times 10^4$)	χ ($ohm^{-1}\ cm^{-1} \times 10^6$)	Λ_M ($ohm^{-1}\ mol^{-1}\ cm^2$)
(VII) $(\eta^5\text{-}C_5H_5)_2NbBr_2Cl$	3.20	27.00	87.09
(VIII) $(\eta^5\text{-}C_5H_5)_2TaBr_2Cl$	4.95	24.20	73.10* (48.73)
(IX) $[(\eta^5\text{-}C_5H_5)_2NbBrCl]^+\ Br_3{}^-$	–	–	[a]
(X) $[(\eta^5\text{-}C_5H_5)_2TaBrCl]^+\ Br_3{}^-$	–	–	[a]
(XI) $(\eta^5\text{-}C_5H_5)_2NbBrCl_2$	1.00	30.50	28.11
(XII) $(\eta^5\text{-}C_5H_5)_2TaBrCl_2$	4.70	20.60	65.74* (43.83)
(XIII) $[(\eta^5\text{-}C_5H_5)_2TaCl_2]^+\ Br_3{}^-$	4.50	35.60	118.65* (79.10)
(XIV) $(\eta^5\text{-}C_5H_5)_2NbClI_2$	4.68	38.50	82.26
(XV) $(\eta^5\text{-}C_5H_5)_2TaClI_2$	4.90	41.00	83.70 (66.20)
(XVI) $[(\eta^5\text{-}C_5H_5)_2NbClI]^+\ I_3{}^-$	4.42	55.00	124.43
(XVII) $[(\eta^5\text{-}C_5H_5)_2TaClI]^+\ I_3{}^-$	5.60	46.10	123.45 (82.30)
(XVIII) $(\eta^5\text{-}C_5H_5)_2NbCl_2I$	6.90	34.50	49.70
(XIX) $(\eta^5\text{-}C_5H_5)_2TaCl_2I$	4.84	23.00	47.50 (36.60)
(XX) $[(\eta^5\text{-}C_5H_5)_2TaCl_2]^+\ I_3{}^-$	4.47	59.00	118.00 (82)
(XXI) $[(\eta^5\text{-}C_5H_5)_2NbCl_2]^+\ I_3{}^-$	3.60	43.00	119.44
(XXII) $(\eta^5\text{-}C_5H_5)_2NbCl_3$	7.90	14.50	18.35
(XXIII) $(\eta^5\text{-}C_5H_5)_2TaCl_3$	4.79	7.70	24.10* (16.07)

[a] In some cases, indicated by an asterisk, the values were obtained by extrapolation from conductivities measured in nitromethane, assuming $\Lambda_{(nitrom)} \times 1.5 = \Lambda_{(acet)}$. [b] Very insoluble compounds which left solid in suspension.

TABLE 3

INFRARED AND NMR[a,c] SPECTRAL DATA FOR (η^5-$C_5H_5)_2MX_2Y$ AND $[(\eta^5$-$C_5H_5)_2MClY]^+$ A_3^- COMPLEXES

Complex	M	X	Y	A	ν(M–Cl) (cm^{-1})	$\delta(^1H)$ C_5H_5 (ppm)
VII	Nb	Br	Cl		290	6.45(s)[b]
VIII	Ta	Br	Cl		325	–
IX	Nb		Br	Br	300	7.14(m)
X	Ta		Br	Br	345	7.07(s)
XI	Nb	Cl	Br		270–290 (br)	6.50(s)
XII	Ta	Cl	Br		290,330	–
XIII	Ta		Cl	Br	295,330	–
XIV	Nb	I	Cl		275	7.06–7.22(m)
XV	Ta	I	Cl		325	7.33–7.13–7.07(m), [6.96(s)[b]]
XVI	Nb		I	I	280	7.04–7.23(m)
XVII	Ta		I	I	330	7.14–7.08(m)
XVIII	Nb	Cl	I		265,285	6.15(m)
XIX	Ta	Cl	I		290,330	7.14(s)
XX	Ta		Cl	I	295,330	7.31–7.21–7.07–7.15(m)
XXI	Nb		Cl	I	280–310 (br)	7.23(m)
XXII	Nb	Cl	Cl		255,280,290	6.52(s)
XXIII	Ta	Cl	Cl.		260,290,310	7.14[b]

[a] The NMR spectra were recorded in acetone-d_6. [b] In chloroform-d. [c] s = singlet; m = multiplet.

Below 350 cm^{-1} the number of bands observed is as expected for the ν(M–Cl) stretching frequencies: three for the trichloro, two for the dichloro and one for the monochloro complexes. We assign these absorptions to the ν(M–Cl) vibrations, and conclude that the remaining M–Br and M–I vibrations must lie below 200 cm^{-1}, that is the lower limit of our instrument. IR data are shown in Table 3.

NMR spectral data

The ^1H NMR spectra could not be recorded in non-polar solvents in which all the complexes studied are insoluble. For complexes soluble in chloroform the spectra show a single resonance for η^5-C_5H_5. The acetone solutions of the complexes which do not dissociate in this solvent ($\Lambda < 50$ ohm^{-1} mol^{-1} cm^2) show a single resonance for η^5-C_5H_5 in the niobium and tantalum derivatives (see Table 3), and the chemical shifts are in agreement with those previously observed for M^V complexes [10]. All the neutral complexes which are dissociated in acetone ($\Lambda > 50$ ohm^{-1} mol^{-1} cm^2), as well as the cationic complexes, show more complex spectra containing several peaks arsing from the presence of the various species formed in solution according to the following equilibria:

$$(\eta^5\text{-}C_5H_5)_2MCl_2X \rightleftarrows (\eta^5\text{-}C_5H_5)_2MCl_2^+ + X^-$$

$$\downarrow\uparrow + S$$

$$(\eta^5\text{-}C_5H_5)_2MCl_2S^+$$

$$(\eta^5\text{-}C_5H_5)_2MClX_2 \rightleftarrows (\eta^5\text{-}C_5H_5)_2MClX^+ + X^-$$

$$\downarrow\uparrow + S$$

$$(\eta^5\text{-}C_5H_5)_2MClXS^+$$

$$(\eta^5\text{-}C_5H_5)_2MCl_2^+ + X_3^- \rightleftarrows (\eta^5\text{-}C_5H_5)_2MCl_2X + X_2$$

$$(\eta^5\text{-}C_5H_5)_2MClX^+ X_3^- \rightleftarrows (\eta^5\text{-}C_5H_5)_2MClX_2 + X_2$$

The complexity of the peaks observed for the iodo complexes is probably due to their higher dissociation and the diversity of species formed in solution.

The single resonances observed for the C_5H_5 confirm the equivalence of both rings, in accord with Hoffman's model [11] which permits the formulation of a structure with the two (cationic) or three (neutral) halogen atoms located on the reflectance plane of both rings.

Experimental

The reactions were carried out under nitrogen using Schlenk-type glassware. Solvents were previously distilled, dried by standard methods, and degassed (N_2). Infrared spectra were recorded using a 505 Perkin–Elmer spectrophotometer between 4000 and 200 cm^{-1} in Nujol. ^{1}H NMR spectra were recorded with a Varian FT 80 instrument in acetone-d_6 and chloroform-d. Analyses were performed with a 240B Perkin–Elmer microanalyser. Halogen determinations were carried out by White's method [12] which gives the total halogen in the sample. The starting complexes $(\eta^5\text{-}C_5H_5)MCl_2$ (M = Nb, Ta) were synthesized as described elsewhere [13,14]. All the yields quoted are relative to the metal-containing starting materials.

Oxidations with chlorine

Suspensions of V and VI (1.00 mmol) were treated with 10 ml of a 0.5 *M* CCl_4 solution of Cl_2 (5.00 mmol). The colour of the solid changed immediately to a yellow green. After stirring for 1 h at room temperature the crystalline solid was filtered off, washed with diethyl ether, dried in vacuo, and characterized as $(\eta^5\text{-}C_5H_5)_2MCl_3$ (M = Nb (XXII), Ta (XXIII)) (90%).

Similar reactions of THF solutions of I, II and III, IV with excess of chlorine gave the same chloro complexes.

Oxidations with bromine

(a) $(\eta^5\text{-}C_5H_5)_2MCl$. Addition of a diethyl ether solution of bromine (0.58 mmol) to solutions of $(\eta^5\text{-}C_5H_5)_2MCl$ [15,7] in the same solvent or in THF produced an immediate change of colour and gave crystalline solids which were identified as $(\eta^5\text{-}C_5H_5)_2MBr_2Cl$ (M = Nb (VII) orange, Ta (VIII) brown-green). The solids were filtered off, washed with diethyl ether and dried in vacuo (60–70%). When the same reaction was carried out using an excess of bromine, orange crystals immediately separated; after filtration, washing with diethyl ether and drying in vacuo these were characterized as $[(\eta^5\text{-}C_5H_5)_2MBrCl]^+ Br_3^-$ (M = Nb (IX), Ta (X)) (90%).

(b) $(\eta^5\text{-}C_5H_5)_2MCl_2$. Addition of a 1.13 *M* solution of bromine in chloroform (0.35 ml, 0.46 mmol) to a suspension of $(\eta^5\text{-}C_5H_5)_2MCl_2$ (0.92 mmol) in diethyl ether (50 ml) gave insoluble crystalline solids. After filtration, the solids were washed with diethyl ether and dried in vacuo. They were identified as $(\eta^5\text{-}C_5H_5)_2MBrCl_2$ (M = Nb (XI) brown orange, Ta (XII) orange) (85%).

When the same reaction of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ was carried out with an excess of bromine, a yellow crystalline insoluble solid appeared almost immediatly. The solid was filtered off, washed repeatedly with diethyl ether, dried in vacuo, and identified as $[(\eta^5\text{-}C_5H_5)_2TaCl_2]^+ Br_3^-$ (XIII) (80%).

No further reaction was observed when an excess of bromine was added to $(\eta^5\text{-}C_5H_5)_2NbCl_2$. The solid isolated from this reaction was identical with that obtained by use of the stoichiometric amount of halogen.

(c) $(\eta^5\text{-}C_5H_5)_4M_2Cl_3$. THF solutions of $(\eta^5\text{-}C_5H_5)_4M_2Cl_3$ (0.90 mmol) were treated with a diethyl ether solution of bromine (0.90 mmol). The violet (Nb) or purple (Ta) colour immediately changed into green and crystalline solids separated out. The solids were filtered off, washed with diethyl ether, dried in vacuo, and identified as $(\eta^5\text{-}C_5H_5)_2MBr_2Cl$. The evaporation of the residual solution gave $(\eta^5\text{-}C_5H_5)_2MCl_2$, which was identified by analysis and comparison with original samples.

When similar solutions of I and II in THF were treated with a larger amount of bromine (1.35 mmol), in molar ratio $Br_2/\text{dimer} = 1.5$, the colour of the solution disappeared. The crystalline products were filtered off, and extracted with chloroform (M = Nb) or acetonitrile (M = Ta). Evaporation of the extracts gave crystalline solids, which were filtered off, washed, dried, and identified as XI and XII. The mother liquors were evaporated to dryness and the solid residues were repeatedly washed, they analysed as complexes VII and VIII.

When the same reactions were carried out with an excess of bromine crystalline solids separated out. They were filtered off and washed with diethyl ether to remove the excess of halogen. The solid obtained for M = Nb was extracted with chloroform until the solution was colourless. The insoluble residue was analysed and identified as IX. Evaporation of the solution gave crystals which were identified as XI.

For M = Ta the solid obtained was extracted with nitromethane. The insoluble residue was identified as X. Concentration of the solution in vacuo gave crystals which were filtered off, washed, dried, and identified as XIII.

Oxidations with iodine

(a) $(\eta^5\text{-}C_5H_5)_2MCl$. When THF solutions of $(\eta^5\text{-}C_5H_5)_2MCl$ (0.58 mmol) were treated with iodine (0.174 g, 0.58 mmol) there was almost instantaneous precipitation of crystalline solids. These were filtered off, washed with diethyl ether, and dried in vacuo. The analytical compositions and spectroscopic data for these solids correspond to $(\eta^5\text{-}C_5H_5)_2MClI_2$ (M = Nb (XIV) brown, Ta (XV) red brown) (80%).

When the same reaction was carried out with addition of an excess of iodine, crystalline dark brown-red solids were obtained, and these analysed as $[(\eta^5\text{-}C_5H_5)_2MClI]^+ I_3^-$ (M = Nb (XVI), Ta (XVII)) (90%).

(b) $(\eta^5\text{-}C_5H_5)_2MCl_2$. Addition of iodine (0.220 g, 0.85 mmol) to a suspension of $(\eta^5\text{-}C_5H_5)_2MCl_2$ (1.70 mmol) in diethyl ether caused a change of colour and separation of crystalline solids. These were filtered off, washed, and dried in vacuo. Their analytical compositions corresponded to $(\eta^5\text{-}C_5H_5)_2MCl_2I$ (M = Nb (XVIII) Ta (XIX)) (80%). The reaction with $(\eta^5\text{-}C_5H_5)_2NbCl_2$ and iodine using chloroform as solvent gave a precipitate of the cationic complex $[(\eta^5\text{-}C_5H_5)_2NbCl_2]^+ I_3^-$, (XXI)), even with a 1/1 I_2/Nb molar ratio. The residual solution yielded unchanged $(\eta^5\text{-}C_5H_5)_2NbCl_2$.

The reaction of $(\eta^5\text{-}C_5H_5)_2MCl_2$ with an excess of iodine in diethyl ether under the conditions described above gave crystals of $[(\eta^5\text{-}C_5H_5)_2MCl_2]^+ I_3^-$ (M = Nb (XXI), Ta (XX)), as indicated by their analytical data and spectra.

(c) $(\eta^5\text{-}C_5H_5)_4M_2Cl_3$. When iodine (0.228 g, 0.90 mmol) was added to solutions of $(\eta^5\text{-}C_5H_5)_4M_2Cl_3$ in THF (0.90 mmol) the violet (Nb) or purple (Ta) solutions

turned green with simultaneous precipitation of crystalline insoluble compounds. These were filtered off, washed with THF, and dried in vacuo. In accord with the analytical data these solids were formulated as XIV as XV. The residual green solutions were concentrated to give crystals of $(\eta^5\text{-}C_5H_5)_2MCl_2$ by comparison with orginal samples. Under the same conditions, addition of iodine to $(\eta^5\text{-}C_5H_5)_4Ta_2Cl_3$ in a molar ratio I_2/dimer = 1.5, gave a pale brown precipitate and a red solution. After filtration the solid was washed with diethyl ether, dried in vacuo, and identified as XIX. The residual solution was concentrated to give crystals which analysed as XV.

When the same reaction was carried out using an excess of iodine a brown red solid separated, and after washing with THF this was identified as XX. The residual red solution was concentrated to 10 ml to give dark red crystals. These were filtered off, washed with diethyl ether several times dried, and identified as XVII, by comparison with an authentic sample obtained as described above.

The same reaction with the niobium complex and excess of iodine in a I_2/Nb molar ratio 1.5 or higher, gave red-brown solids, the composition of which varied with the amount of iodine used, and did not correspond to any reasonable stoichiometry. These solids are probably mixtures of compounds, which could not be separated because of their insolubility.

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